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## Perovskite Crystals: A Bright Future in Solar Technology

### Abstract

Perovskite crystal based solar cells with efficiencies comparable to silicon have been achieved in technical labs. However, the solar cell areas so far are too small for practical applications, and there are still several avenues of experimentation to study the effects of precursor solutions on the final perovskite crystals. The goal of this project was to create low grade cells with greater surface area and investigate the formation of perovskite crystals through a variety of precursor solutions and study their respective semiconductor properties. During this project, cells were constructed with an output voltage of up to 520 millivolts, comparable to traditional silicon solar cells. However the internal resistance of the cells was much too high to produce any sort of usable current or measure any reliable total efficiency. Additionally, the perovskite crystal solar cell was used successfully in improving the overall voltage of a silicon and perovskite tandem cell. The studies showed that rudimentary perovskite crystals could be fabricated at low cost with basic laboratory equipment that give an indication as to which precursor chemicals and concentrations serve as best recipes for final semiconductor crystals. Additionally, the studies show that perovskite semiconductor layers with band gaps of increasing value could be applied to today's silicon cells to improve overall efficiencies.

## Introduction

Energy is essential for daily life, but current energy production relies on non-renewable resources such as oil and fossil fuels. These energy solutions are not only harmful to the environment, they are limited in supply and will eventually be depleted. Unfortunately, current renewable energy solutions are impractical or costly. The ratio of energy production to cost of silicon solar cell is just not great enough to compete with fossil fuels (Agnihotri).

However, in recent years perovskite crystal semiconductors have shown promise in replacing silicon in solar cells. Perovskite crystals are semiconductors that follow the structure  $ABX_3$ , where A is an organic ion with a  $1+$  charge, B is a large cation, and X is a halide (Figure 1). These crystals act similar to other semiconductors such as silicon, however, they are advantageous because they can be constructed using a variety of chemical precursors so that the semiconductor characteristics are altered. For example iodide ions can be replaced by bromide ions so that the overall perovskite crystal will have a higher semiconductor band gap. In addition to tunability, these crystals are easier to manufacture as they do not require vapor deposition manufacturing processes as traditional solar cells do. Perovskite crystals can be created through solution processing, an easier and cheaper method of layering (Jeon). Perovskite crystal solar cells from top research institutions have attained efficiencies matching those of silicon-based solar cells (Grinberg). Theoretically perovskite crystal solar cells could surpass the efficiencies of silicon solar cells. Additionally, perovskite semiconducting crystals with higher band gaps have been investigated for use in tandem with silicon cells to create higher efficiencies (Beal).

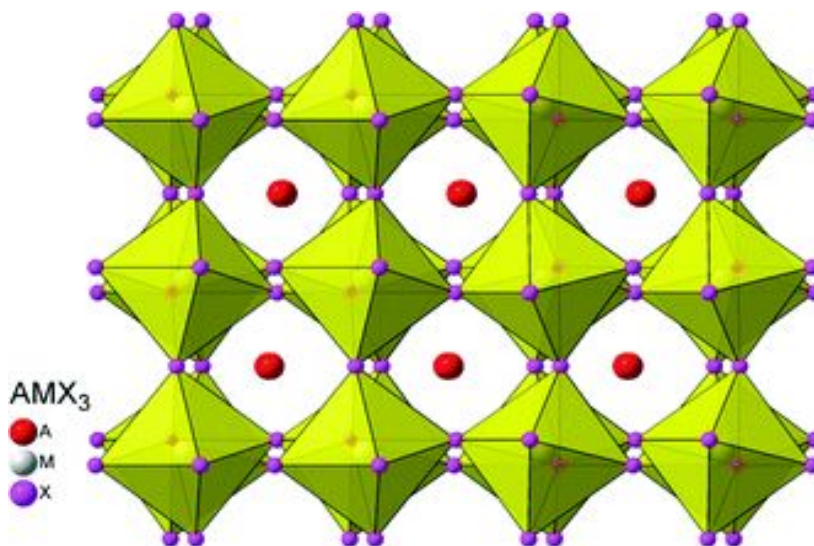


Figure 1: General Perovskite Structure

Formamidinium lead halide perovskite crystals with a 2-to-1 molar ratio iodide to chloride ions were used as a control. The cells were then modified by altering the composition of the precursor solutions in order to achieve higher voltages. For this research the molar ratio of formamidinium chloride to lead (II) iodide within the precursor solutions were altered to achieve crystal structures with variable concentrations of chloride and iodide ions.

Changing the concentrations of the precursor components, and thus the overall composition of the crystal will yield differing semiconductor band gaps. A band gap is the amount of energy a photon of light must transfer to an electron to liberate an electron in the crystal. The more chloride, the higher the band gap. This means that when the cells are exposed to equal amounts of light the solar cells constructed with higher band gap semiconductors would produce higher relative voltages.

This research investigates a change in solar cell voltage as the chloride concentration is increased within the perovskite crystal.

## Materials and Methods

### Perovskite Precursor Solutions:

To create perovskite precursor solutions, formamidinium acetate (Sigma Aldrich, Lot: BCBN5709V) was first dissolved in 8.0 M HCl to create a two to one molar ratio of HCl to formamidinium acetate. This solution was then heated to 50°C with constant stirring and left for ten minutes. Then heat the solution with a hot plate to 100°C and gently boil off the acetic acid and the majority of water. The product, formamidinium chloride (FACl), is purified with two washes of Diethyl Ether (Flinn, Lot: 218041) and recrystallization in anhydrous ethanol (Flinn, Lot: 109788). The product is then filtered and dried in a vacuum oven (GCA, model: Precision) overnight at 60°C. This product is then dissolved with lead (II) iodide (Sigma Aldrich, Lot: MKBV2644V) in Dimethylformamide (DMF, Sigma Aldrich, Lot: SHBD8947V) to achieve solutions of 0.55 M for both solutes (Figure 2). For experimentation, the FACl concentration was doubled and tripled.

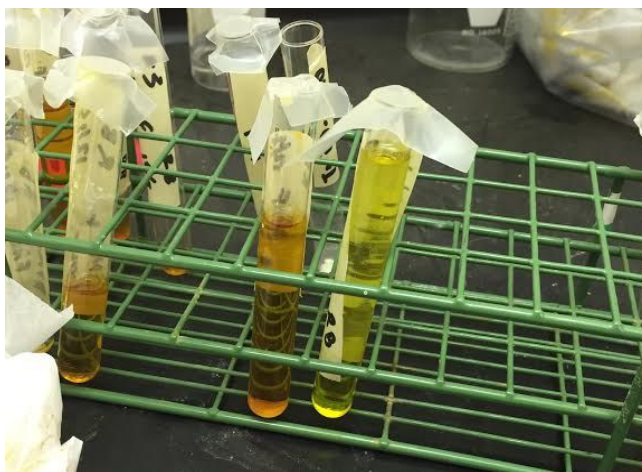


Figure 2: Perovskite Precursor  
Solutions of .55 M FACl and PbI<sub>2</sub> dissolved in DMF.

### Complete Device Construction:

The solar cells were constructed on Fluorine doped Tin Oxide (FTO) glass (Sigma Aldrich, Lot: MKBT8462V) as a conductive and transparent base. The glass was received as 10 mm square sheets, and were cut to 2.5 mm by 3.3 mm using a craft glass scoring device. The glass was then washed in acetone (Flinn, Lot: 207227) and wiped down with KimWipes (Figure 3).

The next layer to be deposited is the  $\text{TiO}_2$ . An acidified solution of 0.2 M titanium isopropoxide (Sigma Aldrich, Lot: SHBG0908V) in anhydrous ethanol is used as the precursor solution. First, a piece of Scotch tape is applied to 8 mm of the conductive side of a piece of FTO glass to create a roughly 25 mm square active area. Then, 50  $\mu\text{L}$  of the titanium isopropoxide solution is pipetted to the surface of the glass, and the glass is spun at 2200 rpm in a centrifuge (San Jose Scientific, model: Mini-Fuge) for 30 seconds (Figure 4). The tape is then removed, and the glass is placed on a hotplate. The hot plate is then turned on and set to  $450^\circ\text{C}$  to anneal the  $\text{TiO}_2$  layer.

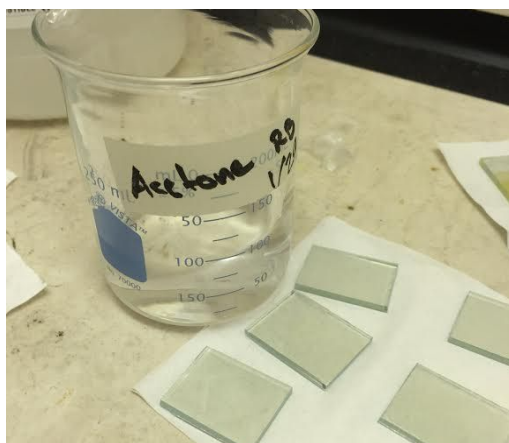


Figure 3: Cleaning FTO glass for use in solar cells

The next layer consists of the perovskite semiconductor. This layer is deposited by first reapplying the tape to the FTO/ $\text{TiO}_2$  glass. Then, once the glass has been preheated to  $100^\circ\text{C}$ , it

is placed in the centrifuge and spun again at about 1000 rpm. 100  $\mu\text{L}$  of perovskite precursor solution is pipetted onto the spinning glass. The glass is left to spin for another 30 seconds. The tape is removed from the glass, and the device is then transferred back to the hot plate and allowed to anneal at  $170^\circ\text{C}$ .

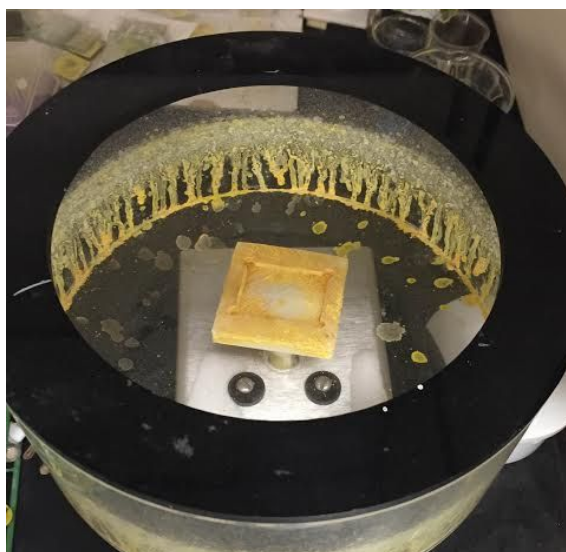


Figure 4: Centrifuge and Adapter for spinning glass

To complete the solar cell, graphite powder (Braun Chemicals) is sprinkled and spread with a glass stir rod on a second piece of FTO glass and then the two pieces of glass are sandwiched together (Figure 5).

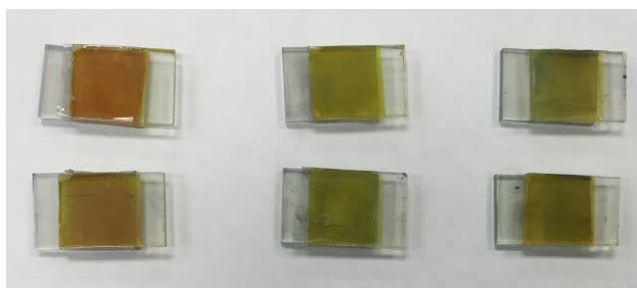


Figure 5: Complete cells created from precursors of  $\text{FACl}$  to  $\text{PbI}_2$  ratios 1:1, 2:1, 3:1

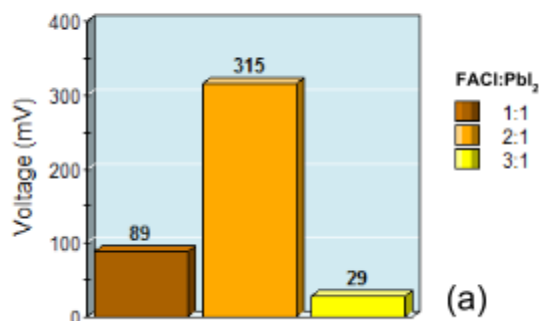
To test the cells, I used a lamp with a 60 W light bulb and a multimeter (RSR, model: MAS830) to test the voltage and short circuit outputs of the solar cells. Additionally, the cells were taken outside in the sun and tested against one another.

### Results

Working perovskite crystal solar cells that reached voltages of up to 520 millivolts were constructed. This is comparable to traditional silicon solar cells. However, the efficiency of the perovskite solar cells was lower than silicon solar cells due to low current output. This is a result of high internal resistance in the cell, which will require further investigation.

The cells which performed best had perovskite crystals formed from the precursor solution with a two-to-one ratio of formamidinium chloride (FACI) to lead (II) iodide (Figure 6). The cells constructed with a three-to-one precursor solution performed with the lowest voltages at on average 29 mV in cloudy conditions and 63 mV in direct sun. The one-to-one precursor solution based cells performed second best with averages of 89 mV and 193 mV in cloudy conditions and direct sunlight respectively. The cells with a two-to-one precursor solution performed optimally, achieving average voltages of 315 mV and 385 mV under clouds and direct sunlight.

**Fresh Cell Averages in Cloudy Conditions**



**2-Day Old Cell Averages in Sunlight**

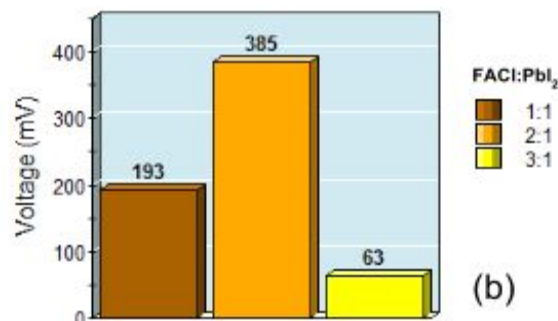


Figure 6: Cell Voltage Averages

Data was collected for the cells tested in (a) cloudy conditions and (b) sunny conditions

The tandem cell showed that when combined, perovskite and silicon semiconductors together can capture light more efficiently than either type by itself (Figure 7). The first bar from the left describes the voltage of the best perovskite cell produced. The second bar is a commercial grade silicon based solar cell. The third bar depicts the cells in series when they are side by side, both absorbing sunlight. The final bar shows the result of placing the perovskite over the silicon cell so that the silicon is only receiving light that has not been absorbed by the perovskite crystal. This shows that when the solar cells are working together in tandem, the overall voltage is greater than either of the cells alone, suggesting potential for more efficient cells.

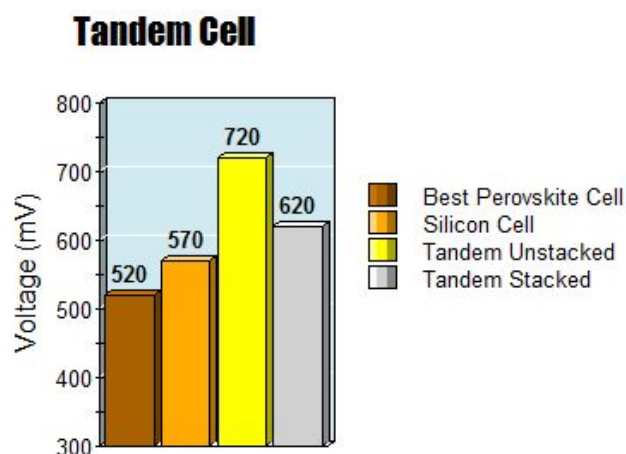


Figure 7: Perovskite-Silicon Tandem Cell

#### Analysis and Conclusion

One hypothesis for the 2:1 ratio  $\text{FACl}:\text{PbI}_2$  generating the highest voltage is that the higher concentration of chloride ions in the precursor solution leads to a higher concentration of chloride ions in the final perovskite crystal. Because the chloride ions have a smaller ionic radius, the band gap of the crystal, or the amount of energy a photon of light must have in order



to liberate an electron, is raised. This increase in energy is seen as an increase in the output voltage of the cell. However, when the molar ratio of the two precursors was greater, e.g. three-to-one, the perovskite crystal could not properly form, resulting in the observed lower voltages seen from cells formed from this precursor solution. A second hypothesis for this result is that the organic halide compounds sublime at similar temperatures to that of the cells being annealed, and therefore must be in excess for a proper one-to-one ratio of lead halide to organic halide and successful formation of the perovskite crystal. This effect could describe the one-to-one precursor solution as creating perovskite crystals with an excessive amount of lead halides acting as inefficiency, thus its lower voltage.

The band gap of a material is the amount of energy needed to liberate an electron, and thus create current. The higher band gap of the perovskite, along with the lower band gap silicon allows the cell to waste less energy from photons of higher wavelengths. This is because the photons of higher wavelengths, and more energy, are able to excite an electron in the perovskite with a higher band gap. The photons of lower energy will pass through the first layer, but will get absorbed by a second or third layer with a lower band gap. This means that capturing higher energy photons does not sacrifice capturing lower energy photons with a lower band gap, or capturing lower wavelengths does not sacrifice the extra energy provided by photons of higher wavelengths.

Despite limited budget (\$400) and a high school laboratory setting, I was able to perform a variety of experiments involving the formation of perovskite crystals. My studies showed that rudimentary perovskite crystals could be fabricated at low cost with basic laboratory equipment. Although these cells do not compare to cells created in better equipped laboratories, their relative

voltage outputs could be measured. These results give an indication as to which precursor chemicals and concentrations serve as best recipes for final semiconductor crystals. Additionally, my results show that perovskite semiconductor layers with band gaps of increasing value could be applied to today's silicon cells to improve overall efficiencies by capturing a greater range of wavelengths produced by the sun with minimal losses.

Further studies could include the use of other organic cations to tune the band gap of the perovskite. Additionally, studies could be performed to raise the band gap of the perovskites through variable halide combinations to create a cell with several band gaps to capture solar energy more efficiently. Finally, the replacement of lead with an ion such as tin would allow for safer, more environmentally friendly devices.

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### Reflection

I chose to do this project because I was interested in both physics and chemistry, and this project incorporated the two. Additionally, the project has great humanitarian value and is still in a cutting edge phase which is exciting to be a part of. I achieved my goals and learned some interesting science along the way. My prediction was close to the actual results but there was somewhat of a surprise for which cell worked the best. This experiment has taught me that scientific studies consist of much more preparation and paperwork than anticipated. I would have liked to learn more about Fermi energy and how electrons flow within materials. It took a very long time to get a cell working, but patience was key to success. If I had to redo the project, I would try more precursor combinations and also investigate the high internal resistance of the cells. I would advise other students to pick a project that is challenging, but also manageable and one where practical data could be collected. I would study other chemical projects such as battery technology. I think this project was important because it taught me several practical lab skills in addition to teaching me to be disciplined in my preparation, records and overall independent motivation to complete the project on a timeline.